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GUM ARABIC FRACTIONATION USING SYNTHETIC MEMBRANES: THE IMPORTANCE OF FOULING

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ABSTRACT

The fractionation of 2 wt% gum arabic using 0.1, 0.5 and 0.8 µm polysulfone (PS) flat sheet membranes is described. Fluxes of between ca. 35 and 80 L m^{-2} h^{-1} were achieved during diafiltration experiments at cross-flow velocities of between 1.0 and 1.6 m s^{-1}. Although high solids rejection is seen by the all three membranes, a high degree of fractionation is also seen, particularly for the 0.1 µm membrane tested, which establishes the principle of this novel membrane application. Rejection of high MW arabinogalactan-protein complex (AGP) is observed with selective transmission of lower MW glycoprotein (GP). Multi-cycle experiments show that flux can be recovered to a high degree after cleaning of the membrane, although with the 0.8 µm membrane, greater fractionation is seen after some fouling has occurred.

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Keywords: Gum arabic, fouling, membrane fractionation

1. INTRODUCTION

Gum arabic has been collected from Acacia trees for centuries due to its array of useful properties. Some of the earliest known uses were as an embalming agent and as a pigment binder and adhesive in paints by the ancient Egyptians (Bonizzoni *et al*., 2011). Gum arabic is still widely used today in the cosmetics, paints and, most notably, in the food and beverage industries.

Gum arabic is a complex polysaccharide exuded by Acacia trees upon damage to the bark in order to seal the wound and prevent water loss or infection. Its tasteless, odourless and often colourless nature and its properties as a natural hydrocolloid with very good emulsifying and stabilising functionality lend it to use in the stabilisation of oil-in-water emulsions, particularly in beverages (Dickinson *et al*., 1989).

The structure of gum arabic is such that it can be chromatographically separated into 3 different fractions: arabinogalactan-protein complex (AGP; MW 1500 kDa; ca. 10% total gum solids), arabinogalactan (AG, MW 280 kDa; ca. 88% total gum solids) and glycoprotein (GP; MW 250 kDa; ca. 2% total gum solids) (Randall *et al.*, 1988; Randall *et al.*, 1989). These values vary greatly, however, depending on tree species, climate, soil conditions etc. The gum used in this work has an average AGP content of 18%.

It has been shown that the highest MW AGP fraction is largely responsible for the emulsifying properties of gum arabic, (Nishino *et al.*, 2012; Randall *et al.*, 1988) so there has been commercial interest in modifying gum arabic to increase its AGP content (Al-Assaf *et*

al., 2007; Fang *et al.*, 2013; Heidebach *et al.*, 2013; Katayama *et al.*, 2012; Sakata *et al.*, 2013; Ward, 2002).

This paper demonstrates the fractionation of gum arabic using synthetic polymeric microfiltration membranes in order to allow AGP enhancement and the development of new gum arabic products for the food industry. The microfiltration of gum arabic is a challenging task, but previous work in the area has shown operating conditions of high cross-flow velocity (CFV) and low transmembrane pressure (TMP) are favourable to minimise fouling and allow the greatest transmission of solids (Bechervaise, 2013; Decloux *et al.*, 1996).

2. MATERIALS AND METHODS

2.1. Diafiltration experiments

Diafiltrations were carried out using 0.1, 0.5 and 0.8 µm polysulfone (PS) membranes (MFG1, GRM-RT5 and GRM-RT8; *Alfa Laval*, Denmark) using a DSS LabStak M10 module with a total filtration area of 336 cm^2 from 4 membranes in series (DSS, Nakskov, Denmark). The maximum feed capacity is 10 L with a dead volume of 700 mL. The membranes were pre-conditioned to remove the glycerine coating by washing with water at 60ºC, 1 bar TMP and CFV of 1.87 ms^{-1} as per the protocol developed in the group (Weis *et al.*, 2005).

Gum arabic was supplied by *Kerry Ingredients and Flavours* (Cam, Gloucestershire, UK) as a milled, raw product from *Acacia Senegal* trees in Sudan. The feed was prepared by dissolving raw gum in water at 40ºC before passing the feed through a 50 µm wound stainless steel pre-filter. All water used was filtered by an Intercept RO-S reverse osmosis system (ELGA ltd, Marlow, UK).

Pure water fluxes (PWF) were measured at 1 bar trans-membrane pressure (TMP), 40ºC and at varying cross-flow velocities (CFVs) for the 0.1 µm membranes and 0.5 bar TMP, 40 ºC and 1.6 ms^{-1} CFV for the 0.5 and 0.8 µm PS membranes. Fouling of the membranes was performed with 50 µm prefiltered 2 wt % gum arabic in water at 40ºC, 1 bar TMP and at varying CFVs for the 0.1 µm membranes and 40 ºC, 0.5 bar TMP and 1.6 ms^{-1} for the 0.5 and 0.8 µm membranes. Permeate flux was measured via a balance and mass readings were taken every 20 s. Permeate samples were taken throughout the experiment and retentate was returned to the tank. Water was added to the feed tank at the same rate as the permeate flux. Permeate samples were dried by rotary evaporation at 55ºC and then in an oven at 55ºC for 24 h.

Cleaning of the membrane was carried out by first rinsing the membrane with water at 40ºC, recording the PWF, cleaning with 0.5 wt% NaOH at 40ºC, 1 bar TMP (0.1 µm) or 0.5 bar TMP (0.5 and 0.8 µm membranes) and a constant CFV throughout, rinsing with water and recording a final PWF.

2.2. Analyses

Dried feed, permeate and retentate samples were weighed and observed solids rejection coefficients were calculated using the equation:

$$R_{coeff} = 1 - \frac{C_p}{C_B} \qquad (1)$$

where C_p is the gum solids concentration in the permeate and C_B is the gum solids concentration in the bulk feed.

The samples were analysed for their C, H and N content using a Carlo Elba Flash 2000 Elemental Analyser configured for % CHN. The % protein can then be estimated from the %N by multiplying by a conversion factor of 6.6, calculated from the amino acid content of gum arabic (Anderson, 1986).

Gum arabic samples and virgin, fouled and cleaned 0.1 μm membranes were analysed by FT-IR using a PerkinElmer 100 FT-IR spectrophotometer with a Universal ATR accessory for sampling.

Top surface images of freeze dried virgin, fouled and cleaned 0.1 μm membranes were taken using a JEOL SEM6480LV instrument after sputter-coating with gold for 2 minutes using an Edwards S150B sputter coater.

Dried samples were dissolved to a concentration of 5 mg mL^{-1} in 20 mM Na_2HPO_4 and sent to *Kerry Ingredients and Flavours* (Cam, Gloucestershire) where gel permeation chromatography (GPC) analysis was carried out. The sample solutions were filtered through 0.2 μm syringe filters before injection into a Malvern GPC-Max instrument fitted with a GE Superose-6 10/300 GL gel column and a triple detection system (right angle light scattering (RALS) / low angle light scattering (LALS), refractive index and UV). The sample run rate was 0.5 mL min^{-1}.

3. RESULTS AND DISCUSSION

3.1. Fractionation of gum arabic

Gum arabic solutions of 2 wt% in water were filtered through 0.1, 0.5 and 0.8 μm polysulfone membranes. The raw gum contained ca. 7 wt% insoluble matter of size > 50 μm, which was removed during the prefiltration. The feed was prepared to be 2 wt% after this pre-filtration.

Figures 1 demonstrates the effect of cross-flow velocity on resistance over time during the diafiltration of 2 wt% gum arabic through a 0.1 μm PS membrane at 40ºC and 1 bar TMP. Five repeats of the filtration at 1.45 m s^{-1} were carried out and the error bars represent ± 1 standard deviation

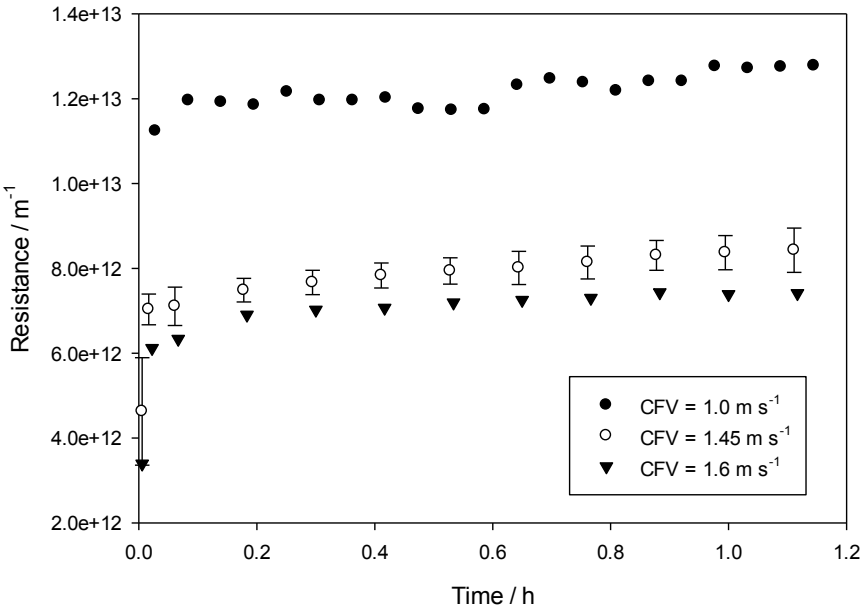

Figure 1: Resistance curves for 2 wt% gum arabic solution at 40ºC and 1 bar TMP. Polysulfone flat sheet membrane: 336 cm^2 area and 0.1 µm pore size. These correspond to average fluxes of 45, 70 and 77 L m^{-2} h^{-1} for 1.0, 1.45 and 1.6 m s^{-1}, respectively.

The cross flow velocities 1.0 ms^{-1}, 1.45 ms^{-1} and 1.6 ms^{-1} correspond to Reynold's numbers through the module channels of 2000, 3000 and 3300 for water and 900, 1300 and 1500 for 2 wt% gum arabic. The membrane resistance was found to be 1.32 x 10^{12} m^{-1} and the resistance of the fouled membrane after rinsing with water is 2.90 x 10^{12} m^{-1}. This gives a value of 1.58 x 10^{12} m^{-1} for the irreversible gum fouling. Figure 1 shows a considerable increase in flux with an increase in CFV. This is possibly due to the increased shear stress in the flow channel at the membrane surface, reducing the effects of fouling and allowing a greater flux. It could also be an effective reduction in feed viscosity due to the increased shear. Gum arabic displays some shear thinning properties so this could be responsible for the increase in flux seen.

As the cross flow velocity of 1.6 ms^{-1} showed the highest flux, this was adopted for further experiments. Experiments with 0.1 µm membranes were carried out at 1 bar TMP but 0.5 bar was used for 0.5 and 0.8 µm filtrations.

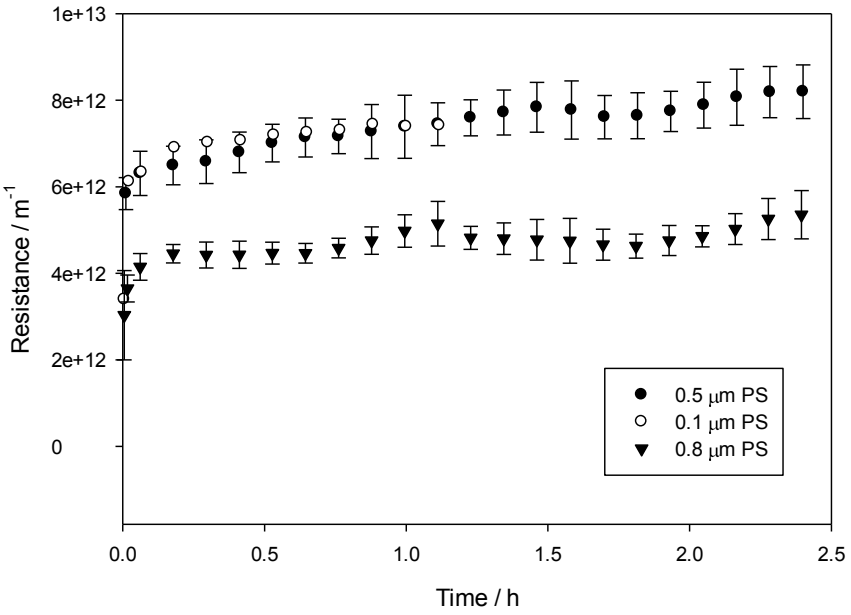

Figure 2: Flux decline curves for the diafiltration of 2 wt% gum arabic through 0.1, 0.5 and 0.8 um PS membranes at 40 ºC and 1.6 ms^{-1} CFV. These correspond to average fluxes of 77 L m^{-2} h^{-1} for 0.1 μm (1 bar TMP), 36 L m^{-2} h^{-1} for 0.5 μm (0.5 bar TMP) and 58 L m^{-2} h^{-1} for 0.8 μm (0.5 bar TMP)

As can be seen from figure 2, the resistance of the 0.5 μm membranes is higher than the 0.8 μm membranes as expected due to the larger pore diameter. However, the 0.1 and 0.5 μm membranes demonstrate similar resistances during filtration. This is suspected to be due to gum aggregates of similar size to the 0.5 μm membrane pore size, causing pore blocking and increasing the resistance compared to the 0.1 μm membranes. Renard *et al.* (2012) studied the structure of gum arabic AGP and found that some larger particles were up to 100 nm in length. Aggregations of several particles of this size could block the pores in 0.5 μm membranes. This is further discussed in section 3.2.

Figure 3 shows how the rejection of solids by 0.1, 0.5 and 0.8 μm PS membranes increases over time during the experiment, as the fouling builds up and adds another layer of filtration. Both the 0.1 and 0.5 μm membranes show rejection of over 95% from the beginning of the filtration, suggesting that the pore size is sufficient to reject a high proportion of the gum particles. The 0.8 μm membrane allows a much greater transmission of solids over the first hour of filtration, which is positive for the overall separation of gum species.

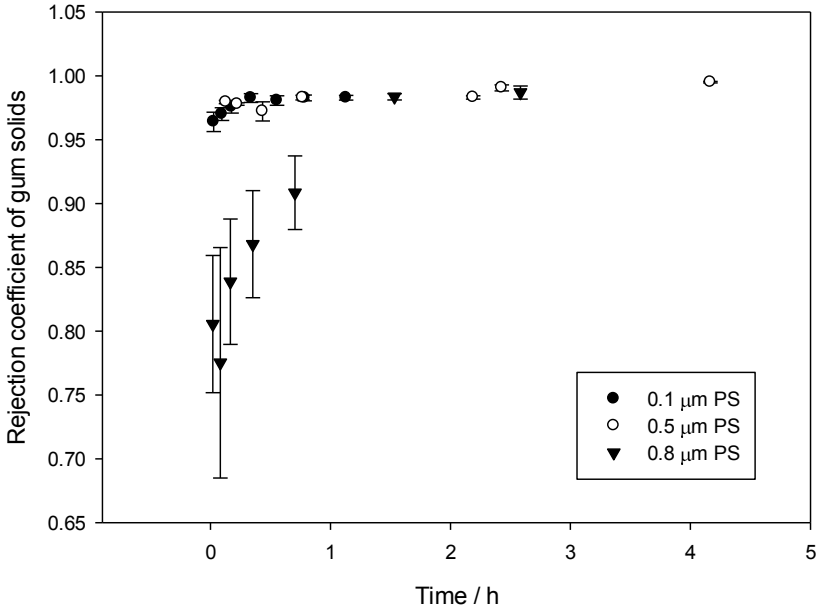

Figure 3: Solids rejection coefficients over time during filtration of 2 wt% gum arabic through 0.1. 0.5 and 0.8 μm PS membranes

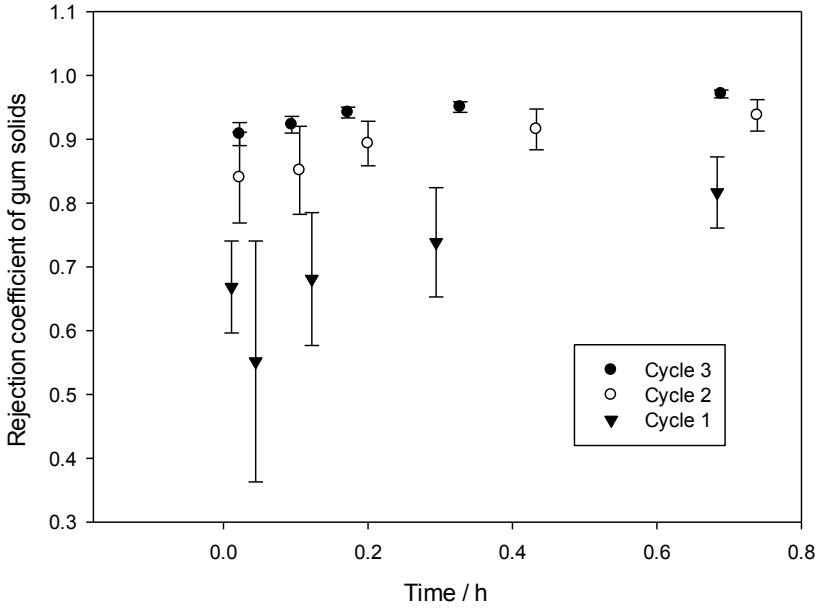

Figure 4: Solids rejection by 0.8 μm membrane during foul-clean cycles 1 (virgin membrane), 2 and 3

Figure 4 shows how the overall gum solids rejection by 0.8 μm membranes increases overtime throughout the fouling experiment and also after each foul-clean cycle. The initial solids transmission seen with a virgin membrane is greater than 30 %, but this reduces to less than 10% after the third cycle. This suggests that a considerable amount on in-pore fouling is building up and is not being removed be the NaOH clean, causing a greater rejection of solids with each cycle.

Permeate and feed samples were taken from each of the experiments, dried and the % protein was measured by elemental analysis and the % AGP by triple detection GPC.

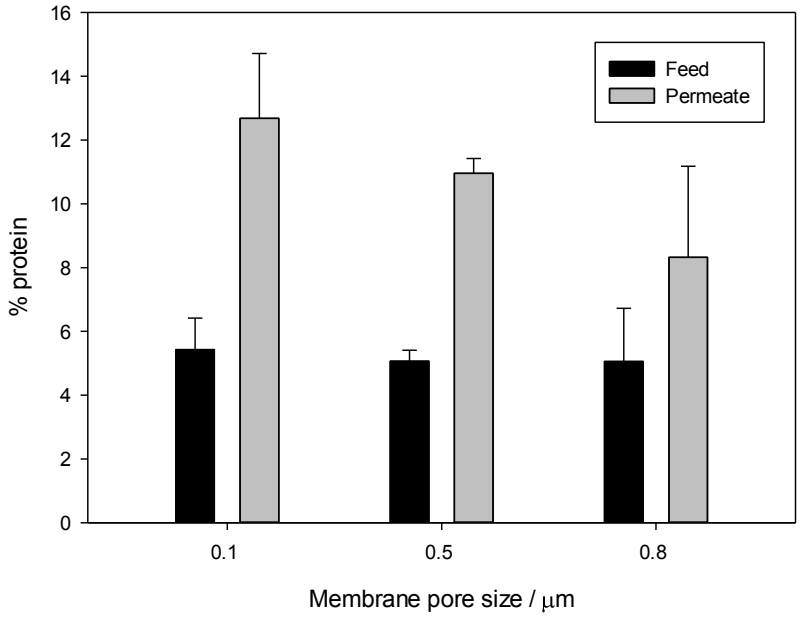

Figure 5: The % protein content of feed and permeate samples from diafiltrations of 2 wt% gum arabic through 0.1, 0.5 and 0.8 μm PS membranes

Figure 5 shows the protein content of the dried, prefiltered feed and permeate samples based on the %N content from elemental analysis. The error bars represent ± one standard deviation. Selective transmission of protein is seen through all three membranes and this is proposed to be due to the low MW glycoprotein (GP) passing through the membrane in preference to the larger arabinogalactan (AG) and arabinogalactan-protein complex (AGP). The percentage protein seen in the permeate reduces as the membrane pore size increases. This is because larger overall solids transmission is seen with the larger pore sizes, and so more of the protein-free arabinogalactan fraction is passing through the membrane, effectively reducing the protein concentration.

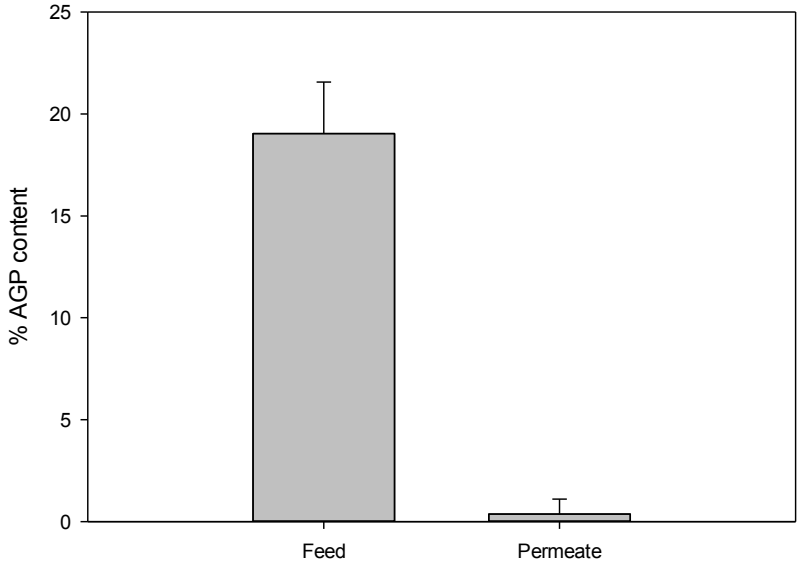

Figure 6: The AGP content of feed and permeate streams for diafiltration experiments carried out using a 0.1 µm PS membrane at 40 ºC

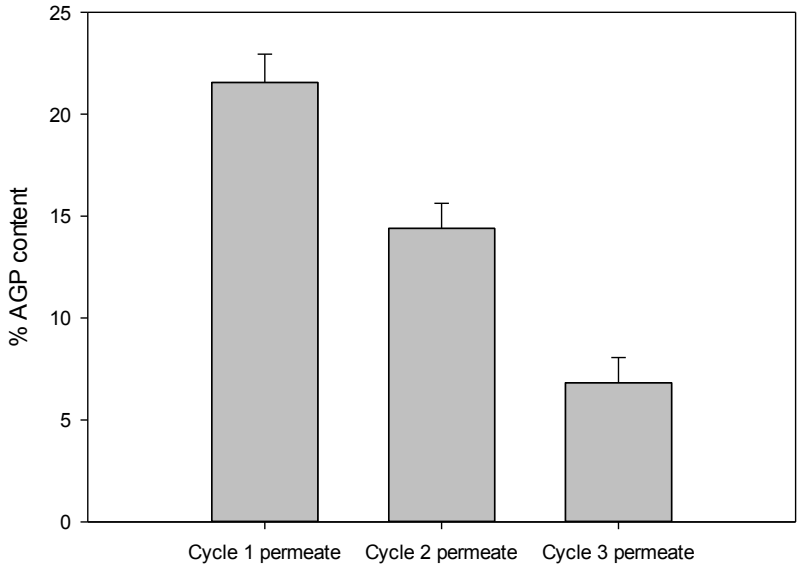

Figure 7: The AGP content of permeate streams from consecutive diafiltration experiments carried out using a 0.8 µm PS membrane at 40 ºC

Figure 6 shows the AGP content of feed and permeate samples taken from 0.1 µm PS diafiltration experiments. It can be seen that this pore size is suitable to reject almost all the AGP within the gum. This is promising; however the low overall solids transmission seen in figure 3 is such that diafiltration experiments would need to be run for a very long time, using large quantities of water in order to sufficiently remove enough of the low MW components and concentrate the AGP.

Figure 7 demonstrates the effect of the build-up of fouling on the 0.8 µm PS membranes which increases the rejection of AGP after 3 foul – clean cycles. A virgin 0.8 µm membrane

(cycle 1) does not selectively reject the AGP but after three cycles a marked increase in AGP rejection is seen. The challenge will be to balance high overall solids transmission with selective rejection of AGP, but these data show that gum arabic fractionation by microfiltration is possible.

3.2. *Multi-cycle experiments*

The diafiltration of 2 wt% gum arabic was repeated over 6 cycles to assess the membrane performance over time and the effectiveness of the cleaning. The process steps were 7-fold and the conditions are detailed in Table 1.

Table 1: Summary of the conditions for fouling/cleaning cycles

	PWF	Foul	Rinse	PWF 2	Clean	Rinse 2	PWF 3
Temperature / ºC	40	40	40	40	40	40	40
TMP / bar	1 or 0.5	1 or 0.5	1 or 0.5	1 or 0.5	1 or 0.5	1 or 0.5	1 or 0.5
CFV / m s^{-1}	1.6	1.6	1.6	1.6	1.6	1.6	1.6
Feed solution	water	2 wt% gum arabic	water	water	0.5 wt% NaOH	water	water
Time / min	30	various	15	20	20	15	30

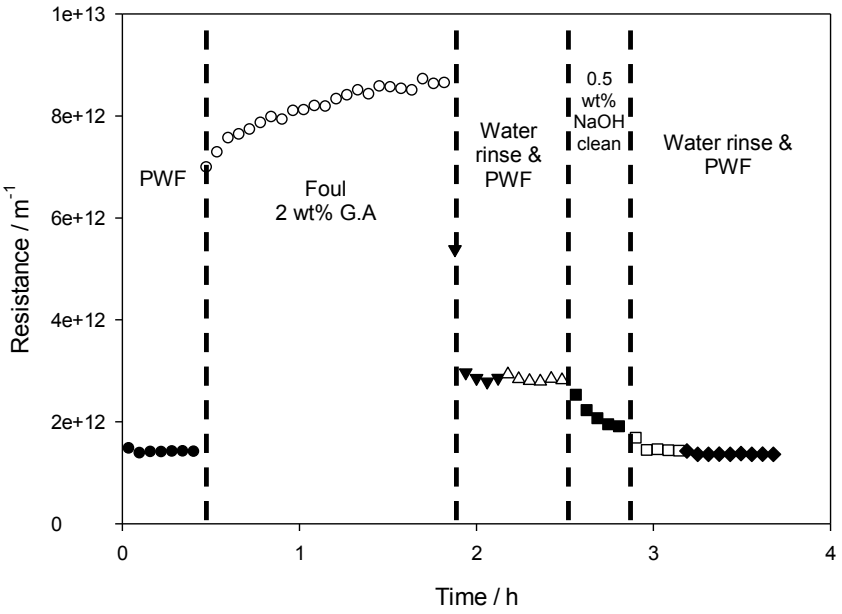

Figure 8: A foul-clean cycle profile for 2 wt% gum arabic using a 0.1 μm PS membrane

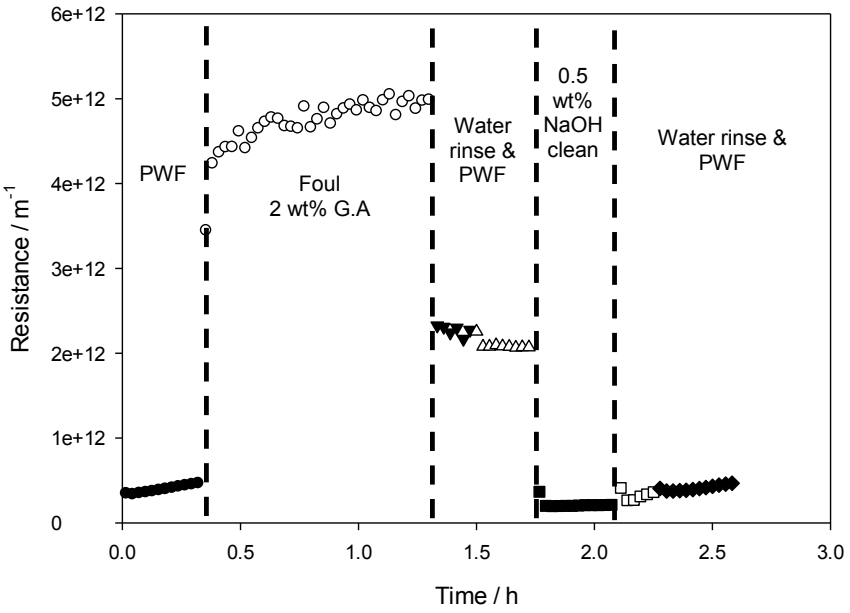

Figure 9: A foul-clean cycle profile for 2 wt% gum arabic using a 0.8 µm PS membrane

Figure 8 shows an example foul-clean profile for 0.1 µm PS membranes, demonstrating good recovery of flux after cleaning as the resistance drops back to the initial value. A similar profile is seen with the 0.8 µm PS membranes in figure 9, although the NaOH clean gives a more dramatic reduction in resistance, which is suspected to be due to a change in the charge of the membrane surface.

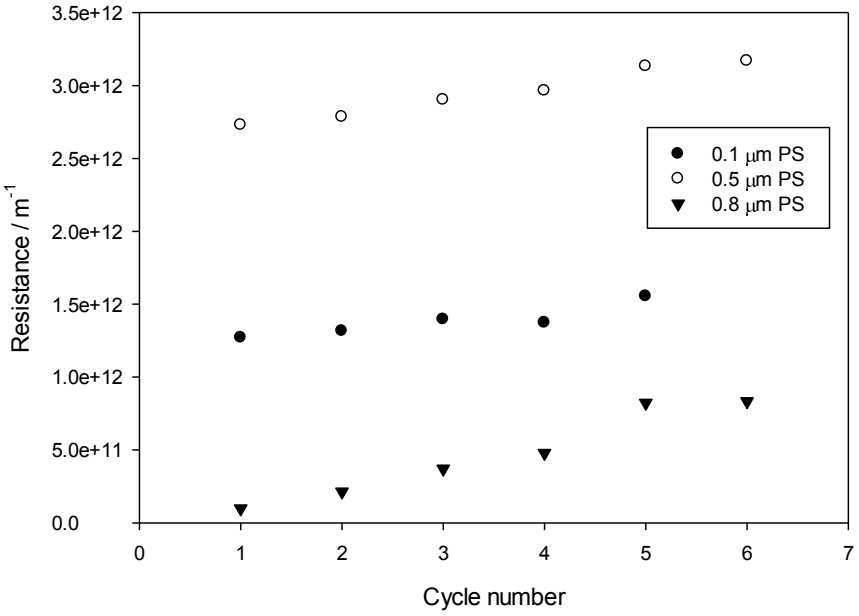

Figure 10: Average PWF measurements with 0.1, 0.5 and 0.8 µm membranes before each fouling cycle

Figure 10 shows how the membrane resistance changes after multiple foul-clean cycles for 0.1, 0.5 and 0.8 PS membranes. Cycle 1 represents the conditioned membrane resistance calculated from the PWF. Cycle 2 is the PWF after the first foul-clean cycle etc. It can be seen that all membranes demonstrate an increase in resistance after each foul-clean cycle, suggesting the cleaning protocol is not sufficient to recover the flux after each cycle. The 0.5 μm membrane shows a greater resistance than the 0.1 μm membrane and this is likely to be due to a greater susceptibility to fouling by residual species in the filtration apparatus. During the conditioning process, all membranes demonstrate a slight reduction in flux, as any foulant trapped within dead zones of the module attach to the membrane, increasing its resistance. This is, however, much more marked for the 0.5 μm membrane. It is hypothesised that the foulant aggreagtes are of a similar size to the pores and therefore this membrane fouls more readily than either the 0.1 or 0.8 μm membranes.

FT-IR was carried out on a virgin (but conditioned to remove the glycerol) membrane, membranes fouled with 2 wt% gum arabic and the cleaned membrane that had undergone 5 foul-clean cycles to determine whether any residual gum arabic fouling is present on the membrane surface after the cleaning process.

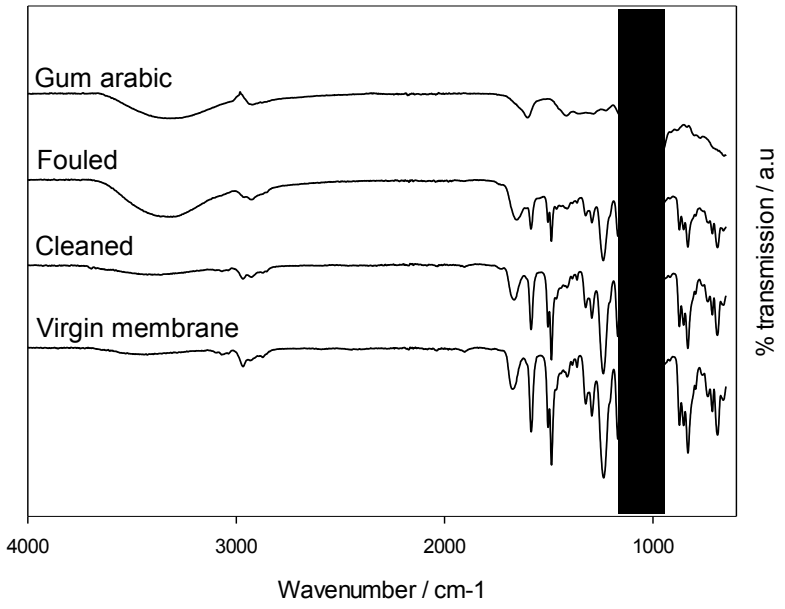

Figure 11. FT-IR spectra for gum arabic (top), 0.1μm PS membrane fouled with 2 wt% gum arabic (second from top), 0.1 μm PS membrane cleaned after 5 foul-clean cycles as above (third from top) and a virgin 0.1 μm PS membrane conditioned to remove glycerol (bottom)

Gum arabic displays typical O-H bending peaks at 1600 cm^{-1}, C-H vibrations between 1400 and 1200 cm^{-1} and intense C-O peaks at 1020 and 976 cm^{-1} as can be seen from figure 11. These peaks become visible in the spectrum for the 0.1 μm PS membrane fouled with 2 wt% gum arabic, although some of the peaks are masked by peaks from the PS. The CO peaks are clearly visible, however, as there is a broadening of the PS peaks at ~1000 cm^{-1}. This broadening is reduced in the cleaned membrane spectrum although the PS peaks appear less sharp than in the virgin membrane spectrum. This is an indication of gum arabic fouling

building up on the membrane after 5 cycles, and that cleaning of the membrane is not complete under the conditions employed.

SEM images were taken of the same 3 virgin, fouled and cleaned membranes. The membranes were freeze-dried prior to analysis so that they retained their structure.

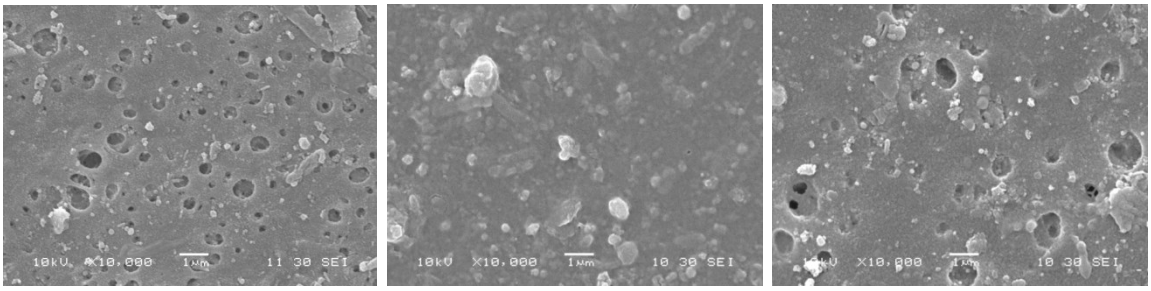

Figure 12. SEM images of the surface of virgin (left), fouled (centre) and cleaned (right) 0.1 µm PS membranes

Figure 12 (left) shows the conditioned, virgin membrane, which shows particles of either loose polymer strands of residual glycerine particles after the conditioning treatment. The fouled membrane (centre) shows blocking of large pore openings on the surface of the membrane by the formation of a cake layer. These openings appear largely cleared of the foulant in the cleaned membrane (right).

It is postulated that at 0.1 µm, the membrane pore diameter is too small to allow transmission of most of the gum species. It is therefore likely that pore blocking within the active layer is minimal, and that cake formation is the dominant fouling mechanism. The presence of a significant cake layer is supported by the electron microscopy images (figure 12). This cake layer is readily removed during the cleaning process, and recovery of pure water flux after each foul – clean cycle is good (ca. 90%).

However, for larger 0.5 and 0.8 µm pore diameter membranes, a greater transmission of gum species is seen. This is likely to lead to more significant pore blocking than was seen for the smaller 0.1 µm pre diameter filters. The cleaning protocol tested appears to be less effective for this type of fouling, as the pure water flux recovery after each cycle is lower, especially for the 0.8 µm membranes (ca. 65%). This effect is particularly seen with the 0.8 µm membrane, as solids transmission values reduce after each fouling – cleaning cycle, whilst fractionation improves.

4. CONCLUSIONS

The fractionation of gum arabic with 0.1, 0.5 and 0.8 µm PS membranes has been shown to be possible. AGP rejection by the 0.1 µm membrane was up to 85 %, although low overall solids transmission was seen. The 0.8 µm membrane showed greater solids transmission but poorer selectivity initially. This improved though, as a fouling layer built up on the membrane after several foul – clean cycles. Preferential transmission of low MW glycoprotein was observed for all membranes. Multi-cycle experiments have shown good recovery of flux after 6 cycles, although some residual fouling, particularly with the larger pore sized membranes does appear to be present.

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